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II. The Drude Method Applied to Aqueous Solutions of Potassium Chloride

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
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Dielectric Constant Studies. II. The Drude Method Applied to Aqueous Solutions of Potassium Chloride

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(Received August 30, 1933)

This paper is an experimental comparison of several adaptations of the Drude method as applied to conducting solutions. With three distinct types of detecting device, results for the dielectric constant of water and of water-alcohol mixtures agreed within experimental error. When, however, the same apparatus was applied to measurements

with KCl solutions, different results were obtained with each. This indicates that any apparent change in the dielectric constant of electrolytic solutions, as observed by the Drude method, must depend in whole or in part upon the characteristics of the apparatus.

WITH the intention of measuring the dielectric constants of some electrolytic solutions, the authors constructed several modifications of the Drude apparatus. Comparison of the results obtained with these modifications, by using the same electrolyte, indicated a pronounced ambiguity, which, judging from our own experience and from work reported in the literature, seems to be characteristic, also, of the results of other methods.

Of the methods which have been employed for the measurement of dielectric constant of leaky dielectrics, the Drude method has much in its favor. It has, however, three obvious limitations: first, it requires a large amount of material; second, the material used must be in the liquid state; and third, because of the length of the tube required it can be operated only at very high frequencies. On the other hand, it appears to possess the best theoretical foundation, since the dielectric constant of a leaky dielectric is defined directly by the Maxwell equation:

$$(\epsilon\mu/c^2)\partial^2 E/\partial t^2 + (4\pi\rho\mu/c^2)\partial E/\partial t = \nabla^2 E,$$

where ρ is the conductivity of the medium, ϵ its dielectric constant, μ its magnetic permeability, c the velocity of light and E the electric intensity. The method has been applied to electrolytic solutions by several investigators, among whom may

be mentioned Drude,¹ Deubner,² Devoto,³ Drake, Pierce and Dow.⁴ In general the results with this method were interpreted as indicating practically no change of dielectric constant with concentration of the electrolyte. (An exception might be noted in the result of Deubner² for CuSO_4 ; he found a decrease in the dielectric constant with an increase in concentration, a result in disagreement with the earlier observations of Drude on the same material.) This, it will be noted, is at variance with the results of other methods, some of which⁵ seem to indicate an increase and others⁶ a decrease in the dielectric constant with concentration of electrolyte.

The essentials of the Drude apparatus are a source of high frequency oscillations, a Lecher wire system and a means of detecting the nodal or antinodal points on the wires.

The high frequency oscillations used by Drude¹ and other earlier workers consisted of damped waves. Deubner,² and Drake, Pierce and Dow⁴ employed oscillations from the usual re-

¹ Drude, *Zeits. f. physik. Chemie* **23**, 267 (1897).

² Deubner, *Ann. d. Physik* **84**, 429 (1927).

³ Devoto, *Gazz. chim. ital.* **60**, 208 (1930).

⁴ Drake, Pierce and Dow, *Phys. Rev.* **35**, 613 (1930).

⁵ Wien, *Ann. d. Physik* (5) **11**, 429 (1931). Lattey and co-workers, *Phil. Mag.* **7**, 985 (1929); **11**, 997 (1931); **12**, 1111 (1931); **13**, 441 (1932). Jezewski, *Phys. Zeits.* **34**, 88 (1933).

⁶ Walden, Ulich and Werner, *Zeits. f. physik. Chemie* **129**, 389 (1927). Shanke and Schreiner, *Phys. Zeits.* **28**, 597 (1927). Sack, *Phys. Zeits.* **28**, 199 (1927). Bramley, J. Frank. Inst. **205**, 649 (1928).

* Rewritten from a thesis presented by J. Gilbert Malone in partial fulfillment of the requirements for the degree of Doctor of Science at the University of Michigan.

generative thermionic oscillators, while Devoto³ used oscillations from a Barkhausen-Kurtz generator.

The earlier form of the Lecher wire system used by Drude and by Deubner consisted of the conventional arrangement of two parallel wires surrounded by the medium to be investigated. Devoto³ modified the Drude method by the use of a single wire instead of two. Drake, Pierce and Dow⁴ substituted a concentric cylinder system for the parallel wires.

The detecting device used by Drude was a neon bulb, Devoto and Deubner employed a milliammeter of the thermocouple type, while Drake, Pierce and Dow used the reaction of the Lecher wire system on the oscillator to give the nodal points.

The present authors have employed two types of Lecher wire systems, three distinct types of detection and a source of undamped waves.

EXPERIMENTAL

A diagram of the apparatus is shown in Fig. 1. For measurements of the wave-length in air, two wires, (see Fig. 1a) W and W' , 1.5 inches apart, were mounted vertically between the floor and ceiling of the room, the ends being secured by Bakelite supports. The lower ends were connected to the terminals of a Weston milliammeter while a shorting bridge B , constructed of metal and Bakelite and provided with spring contacts, was movable on the wire system. The oscillator was placed on the floor within a foot or two of the wire system, and the positions of the nodal points of the waves induced on the wires were determined by moving the bridge and noting the points of maximum current as shown by the milliammeter.

For the measurement of the wave-length in liquid media a similar arrangement (Fig. 1c) was employed except that in this case the wires were $\frac{1}{2}$ inch apart and were surrounded for the greater part of their length by a glass tube 5 inches in diameter and about 7 feet long. The lower end of the tube was closed by a rubber stopper, through which the wires protruded to the milliammeter. The connections of the wires at the upper end of the tube are shown in the figure. In order to maintain a constant temperature, the liquid was

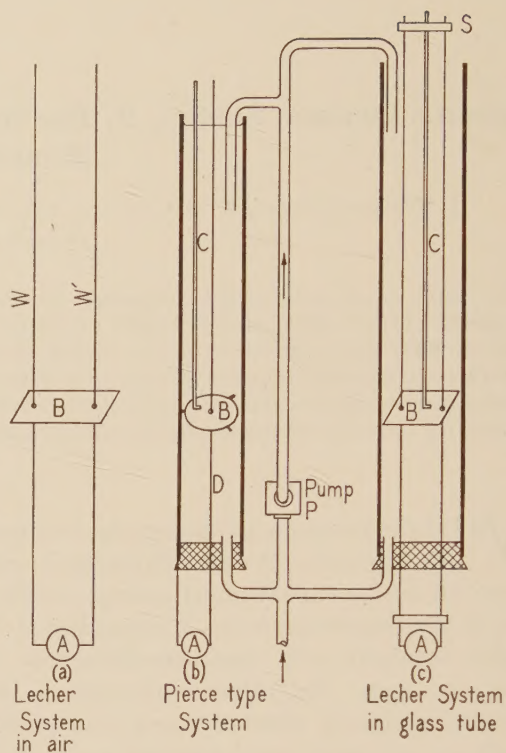


FIG. 1. Diagram of apparatus.

circulated by means of an electrically driven pump connected with glass and rubber tubing to the top and bottom of the large glass tube. Heating units were located around the tube and the whole was heat insulated. A thermometer in one of the glass connections from the pump gave a convenient means of reading the temperature. The shorting bridge B providing reflection of the wave within the tube was moved from the top by means of a calibrated Bakelite rod (C), which, by means of a vernier, was read to a precision of 0.01 cm. The ammeter at the bottom was read from the top by means of a telescope.

In addition to the glass tube apparatus just described the system of Drake, Pierce and Dow was also employed. This apparatus (Fig. 1b) consisted of a brass tube 7.5 feet long and 2.5 inches in diameter, closed at the lower end by a rubber stopper and containing an axially located phosphorbronze wire D . The circulation of the liquid and the detecting arrangement used here were of the same type as described above for the glass tube.

All wires, the interior of the metal tube, and the exposed parts of the pump were heavily silver plated, and where parts were exposed to considerable wear solid silver was used. In the first detecting arrangement employed in the present work, the ammeter was fixed at the generator end of the wire system and the shorting bridge moved to locate the maxima. This arrangement has been used by Laville.⁷

The undamped waves employed were generated by a vacuum tube oscillator. The measurements were carried out in the following manner. The wave-length in air was first determined with the auxiliary wire system. In the early part of the work these measurements were checked on each of the other systems, but it soon became evident that this was not necessary. Without changing the generator the wave-length in the liquid was then determined with either the glass or brass tube arrangement. The wave-length in air was remeasured at the end of each experiment to make sure that it had not changed. The ratio of the half wave-lengths thus obtained was taken as the index of refraction, n . For nonconductive media $n^2 = \epsilon$.

With the object of comparing the two tubes and of testing the accuracy of the apparatus, some preliminary measurements were made with water and with water-alcohol mixtures. The results with water are shown in Table I. It will be noted that the glass tube gave slightly lower values for ϵ than the concentric cylinder system. This result was attributed to the fact that a sensible portion of the field lay outside the water in the tube. Support was given to this explanation by the still lower value of 72.90 obtained when the Lecher wires were further apart.

The results obtained with alcohol-water mixtures covering the entire concentration range agreed satisfactorily with those of Wyman⁸ the average deviation being 0.75 percent.

It seemed that the above determinations established the reliability of the apparatus for work with non-electrolytes and accordingly some work on electrolytes was attempted. For these measurements, KCl and CuSO₄, representing two types of ions, were selected, solutions of these

TABLE I. Comparison of parallel wire and concentric tube systems.

Temp.	$\lambda/2$ air	$\lambda/2$ in liquid	ϵ at T	ϵ at 25°C
20.4	176.2	<i>g</i> 19.74 <i>m</i> 19.67	79.68 81.25	78.03 78.59
16.6	176.2	<i>g</i> 19.55 <i>m</i> 19.54	81.23 81.31	78.61 78.69
water changed				
21.2	176.2	<i>g</i> 19.74 <i>m</i> 19.74	79.68 79.68	78.36 78.36
24.2	176.2	<i>g</i> 19.86 <i>m</i> 19.85	78.71 78.79	78.36 78.54
29.0	176.2	<i>g</i> 20.06 <i>m</i> 20.04	77.15 77.31	78.59 78.75
water changed				
23.3	176.1	<i>g</i> 19.85 <i>m</i> 19.77	78.70 79.34	78.09 78.73
24.0	176.2	<i>g</i> 19.92 <i>m</i> 19.87	78.24 78.64	77.88 78.28
23.2	176.2	<i>g</i> 19.86 <i>m</i> 19.81	78.71 79.11	78.11 78.51
30.4	176.2	<i>g</i> 20.15 <i>m</i> 20.13	76.46 76.61	78.40 78.55
water changed				
20.1	176.2	<i>g</i> 19.69 <i>m</i> 19.67	80.08 80.24	78.22 78.48
22.6	176.2	<i>g</i> 19.78 <i>m</i> 19.77	79.35 79.43	78.49 78.57
26.5	176.2	<i>g</i> 19.96 <i>m</i> 19.95	77.93 78.00	78.47 78.68
water changed				
23.6	176.2	<i>g</i> 19.86 <i>m</i> 19.80	78.71 79.19	78.20 78.69
26.0	176.2	<i>g</i> 19.94 <i>m</i> 19.93	78.01 78.16	78.43 78.52
25.0	176.2	<i>g</i> 19.92 <i>m</i> 19.86	78.24 78.71	78.24 78.71

Average as measured by glass tube 78.36.

Average as measured by metal tube 78.58 at 24°C.

m is value measured by metal tube system.

g refers to the glass container and the Lecher wire system.

salts having been frequently investigated by others. The results obtained are given in Fig. 2. The values given are for n^2 ; since in this work we are concerned only with relative values, no attempt has been made to apply a correction for conductivity, which would be uncertain at best. It will be noted that the values show a decided decrease with increase in concentration, whereas others, working with the Drude method, as was pointed out earlier, have found practically no effect on the dielectric constant due to electro-

⁷ Laville, *Les Ondes Electriques Courtes*, p. 126, R. Mesny, Paris (1927).

⁸ Wyman, J. Am. Chem. Soc. **53**, 3292 (1931).

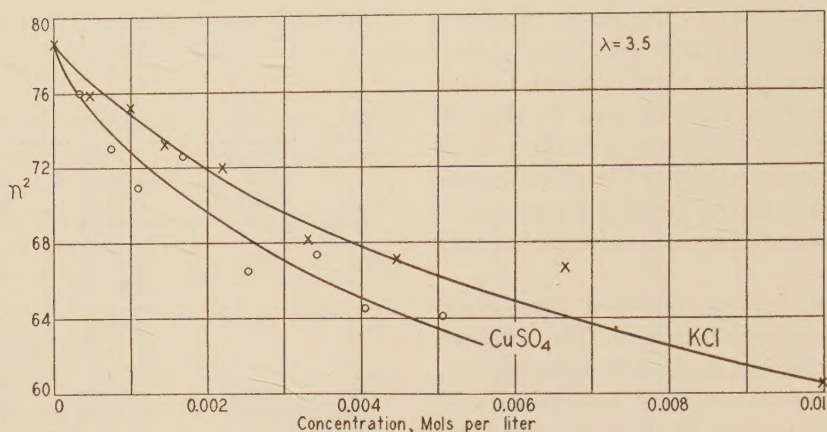


FIG. 2. n^2 against concentration for electrolytic solutions.

lytes. These discrepancies may be due at least in part to differences in the equipment used. For instance, the various detecting devices no doubt introduce complicating factors in the application of simple theory, factors which may produce results differing both in magnitude and direction from the correct n^2 value. No quantitative theoretical relationship taking these factors into account has so far been developed.

An experimental study of this question was undertaken by the use of two additional types of detecting device. The first was a voltmeter constructed from a UX222 tube and which had been found satisfactory in connection with some resonance work being carried on in this laboratory. The potentials across the input end of the apparatus could be followed by the changes in the plate current of the tube. The grid was connected to the center wire, forming the inner cylinder of the concentric cylinder system, while the filament was connected to the tube by a short heavy wire and was also grounded. This apparatus functioned very well but it was more sensitive to changes in the surroundings than was the case with the previous detector. With this device, the values obtained for water and for one concentration of ethyl alcohol, 34.5 percent, were consistent with those previously obtained. While in these cases the position of the nodes was altered by the substitution of the new detector, the distance between nodes was the same as before. However, the precision was much less than in the case already described. With electrolytes, however, greatly different results were obtained.

Although the results were not very reproducible, a large and fairly uniform *increase* of n^2 with increasing concentration was observed.

A third detecting device was used, depending upon the reaction of the measuring system upon an additional resonant circuit, the changes in which were observed by means of the vacuum tube voltmeter which was inserted across the input terminals. With this arrangement the nodes in the measuring circuit could be observed by noting the points of maximum reaction on the added circuit as shown by the plate current of the vacuum tube in it. Here again the values observed for alcohol and water were consistent with those obtained in the preceding cases, but the values observed for KCl solutions were quite different. The n^2 values calculated from the observations show again an *increase* with increasing concentration of electrolyte, but less than in the preceding case. The limited extent of this increase indicates that there is little change in dielectric constant when it is calculated from n^2 by means of the Maxwell relationship for a leaky dielectric. Such a result approximates that obtained by Drake, Pierce and Dow using a similar method.

The last two procedures were not carried to high refinement by the present authors and although they gave fairly consistent results they were particularly sensitive to changes of capacitance in the surroundings.

It is generally realized that the problem of the dielectric constant of electrolytic solutions is highly complex. This was the conclusion arrived

at by Debye⁹ in 1929 as a result of a critical study of the literature up to that time. As stated in the first paper of this series, the authors undertook this work in an attempt to clarify this situation. The results show, however, that the problem is even more complex than has been realized. The measurements reported in this and the preceding paper indicate that while self-consistent results can be obtained even for electrolytes by each of the various methods in the hands of different observers, there is no conformity in the results of different methods, even when employed

by the same investigator.¹⁰ Since, as has been pointed out, these discrepancies do not appear in the case of non-electrolytic solutions, it is evident that conductivity is responsible for the anomalous results obtained, and that its effect is different with different methods. The few attempts which have been made to treat this effect theoretically are inadequate, and until an adequate treatment has been made the changes observed by any method cannot be regarded as representing true changes in dielectric constant.

⁹ Debye, *Polar Molecules*, Chapter VI, Chemical Catalog Co., New York (1929).

¹⁰ cf. Lattey, *Phil. Mag.* **41**, 829 (1921); **12**, 1111 (1931); **13**, 444 (1932).



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